A NEW MODEL FOR THERMAL VOLATILIZATION OF
SOLID PARTICLES UNDERGOING FLASH-PYROLYSIS

J. Villermaux, B. Antoine, J. Lédé and F. Soulignac

Laboratoire des Sciences du Génie Chimique, CNRS-ENSIC Nancy-France

Many industrial processes involve the consumption of solid particles immersed in a reacting medium. Among these, the gasification of coal and biomass in fixed, fluidized or moving beds is of special interest. A great number of models describing gas-solid reactions can be found in the literature [1] [2] [3] [4] [5]. Models dealing with the thermal volatilization of a solid controlled by heat transfer between the surrounding medium and the inner volume of the particle are more scarce. In addition, existing models often rely on the concept of a "surface reaction", which is questionable, because deeper layers also contribute to the reaction as heat penetrates into the solid.

We propose below a new model describing the volatilization of a solid by thermal penetration (VTP model). This model was initially imagined for interpreting flash-pyrolysis of sawdust particles. Actually, it could be applied to any kind of solid reactions where volatilization is controlled by heat conduction from the outer surface. Only a few preliminary but significant results are presented in this paper. More extensive and accurate simulations will be published later.

1. Assumptions and model equations

The basic assumptions of the model are :

- The solid is homogeneous and its mean density ρ is constant and independent of temperature.

- Heat transfer takes place by conduction in the solid, heat conductivity λ and heat capacity c_p are assumed to be constant.

- The rate of volatilization of the solid is $\mathcal{R}$. $\mathcal{R}$ is the mass of solid transformed into gas per unit time and per unit solid volume. $\mathcal{R}$ increases with temperature according to Arrhenius law $\mathcal{R} = k_o \exp(-E/R_g T)$.

- The reaction is endothermic, the reaction enthalpy per unit mass of solid is $\Delta H > 0$ (the case of $\Delta H < 0$ can also be treated by this model, but it will not be discussed here). It is assumed that $\Delta H = \Delta H_1 + \Delta c_p(T - T_1)$ where T_1 is a reference temperature.

- The gaseous products escape freely towards the surface without any diffusional resistance (this is possible if the remaining solid has a porous structure allowing free gas permeation).

- However, it is assumed that the remaining solid shrinks so that it conserves a constant density. The result is that, seen from the center, all the points in the solid seem to move nearer to each other. Conversely, seen from the surface, it is the center which seems to come nearer. This linear shrinking velocity will be denoted as u.

- The solid particle is initially at constant temperature T_o where the reaction is negligible. It is suddenly immersed in a hot medium. Four kinds of boundary conditions can be imagined :

a) Constant surface temperature $T_s = T_p$ (Cauchy condition).

b) Constant surface heat flux q_o

c) Convective heat transfer from a gas at constant temperature T_p (Fourier condition)

d) Radiative heat transfer from a wall at constant temperature T_p.

Only conditions a) and c) will be considered here.

- The particles may have different initial shapes. The case of infinite slabs and spheres will be treated below but this is not a limitation of the model. Actually, a unified treatment valid for any shape can be developed, especially in the so-called "ablation regime". The situation is very similar to that encountered in the study of diffusion-controlled reactions in catalyst pellets.

- Volatilization thus causes shrinking along one single dimension. One wants to calculate the decay of thickness L as a function of time and the time t_F for total consumption of the particle.

Depending on the problem, coordinate axis may be attached to the outer surface of the particle (Oz normal to the surface, directed towards the center and thus moving as volatilization proceeds). This is especially convenient for a slab and for the study of the "ablation regime". This will be referred to below as convention I. Conversely, the axis may be attached to the center of the particle (Or normal to the outer surface); this is more convenient for a sphere and a cylinder, and will be referred to below as convention II.

At any time, there exist a temperature profile $T(z,t)$ or $T(r,t)$ and a shrinking velocity profile $u(z,t)$ or $u(r,t)$. The mass and energy balances are easily written as follows:

Dimensional units, infinite slab, convention I:

Mass balance:

$$\rho \frac{\partial u}{\partial z} + \mathcal{R} = 0 \tag{1}$$

$$\mathcal{R} = k_o \exp(-E/R_g T) \tag{2}$$

Initial and boundary conditions:

$$\left. \begin{array}{l} t = 0, \ u = 0, \ L = L_o \\ z = 0, \ u = 0 \\ z = L, \ u_L = \frac{dL}{dt} < 0 \end{array} \right\} \tag{3}$$

Heat balance:

$$\lambda \frac{\partial^2 T}{\partial z^2} = \mathcal{R} \Delta H + \rho u \, c_p \frac{\partial T}{\partial z} + \rho c_p \frac{\partial T}{\partial t} \tag{4}$$

Initial and boundary conditions:

$$\left. \begin{array}{ll} t = 0, \ T = T_o \\ z = 0, \quad \text{a) } T = T_p & \text{b) } - \lambda\frac{\partial T}{\partial z} = q_o \\ \text{c) } - \lambda \frac{\partial T}{\partial z} = h(T_p - T) & \text{d) } - \lambda \frac{\partial T}{\partial z} = \epsilon\sigma(T_p^4 - T^4) \\ z = L \quad \frac{\partial T}{\partial z} = 0 \end{array} \right\} \tag{5}$$

Infinite slab $(p = 0)$, infinite cylinder $(p = 1)$, sphere $(p = 2)$, convention II:

$$\frac{1}{r^p} \frac{\partial}{\partial r} (r^p \rho u) + \mathcal{R} = 0 \ , \ \mathcal{R} \text{ given by (2)} \tag{1'}$$

Initial and boundary conditions :

$$\left. \begin{array}{l} t = 0, \ u = 0, \ r = R_o \\ r = 0, \ u = 0 \\ r = R, \ u_R = \frac{dR}{dt} < 0 \end{array} \right\} \tag{3'}$$

391

Heat balance::

$$\frac{\lambda}{r^p} \frac{\partial}{\partial r} \left[r^p \frac{\partial T}{\partial r} \right] = \mathfrak{R} \, \Delta H + \rho u c_p \frac{\partial T}{\partial r} + \rho c_p \frac{\partial T}{\partial t} \tag{4'}$$

Initial and boundary conditions:.

$$t = 0, \ T = T_o; \ r = 0, \ \frac{\partial T}{\partial r} = 0$$

$$\left. \begin{array}{ll} r = R \quad \text{a) } T = T_p & \text{b) } \lambda \frac{\partial T}{\partial r} = q_o \\[2mm] \text{c) } \lambda \frac{\partial T}{\partial r} = h(T_p - T) & \text{d) } \lambda \frac{\partial T}{\partial r} = \varepsilon\sigma(T_p^4 - T) \end{array} \right\} \tag{5'}$$

It is interesting to write the model equations in reduced form. For the slab case, convention I, dimensionless quantities are defined as follows: $x = z/L_o$, $\theta = t\mathfrak{R}^*/\rho$, $v = \rho u/(L_o \mathfrak{R}^*)$, $Y = T/T^*$, $W = \mathfrak{R}/\mathfrak{R}^*$, $A = E/(R_g T^*)$, $M = \mathfrak{R}^* L_o^2 c_p/\lambda$, $\ell = L/L_o$, $H = \Delta H_1/(c_p T^*)$, $K = \Delta c_p/c_p$, $B = hL_o/\lambda$, $Q_o = q_o L_o/(\lambda T^*)$, $S = \varepsilon\sigma L_o T^{*3}/\lambda$. ($R_g$ is the gas constant).

T^* is a reference temperature (in the numerical examples treated here $T^* = T_1 = T_p$), and $\mathfrak{R}^*$ is the rate of reaction at T^*.

Equations (1) to (5) are then written:

$$\frac{\partial v}{\partial x} + W = 0 \tag{6}$$

$$W = \exp\left[-A\left(\frac{1-Y}{Y}\right)\right] \tag{7}$$

$$\theta = 0, \ v = 0; \quad x = 0, \ v = 0; \quad x = \ell, \ v = \frac{d\ell}{d\theta} \tag{8}$$

$$\frac{1}{M} \frac{\partial^2 Y}{\partial x^2} = (H + K(Y - Y_p))W + v \frac{\partial Y}{\partial x} + \frac{\partial Y}{\partial \theta} \tag{9}$$

$$\left. \begin{array}{ll} \theta = 0, \ Y = Y_o & \\[1mm] x = 0 \quad \text{a) } Y = Y_o & \text{b) } -\frac{\partial Y}{\partial x} = Q_o \\[2mm] \quad\quad \text{c) } -\frac{\partial Y}{\partial x} = B(Y_p - Y) & \text{d) } -\frac{\partial Y}{\partial x} = S(Y_p^4 - Y^4) \end{array} \right\} \tag{10}$$

A similar reduction can be performed on equations (1') to (5'), the characteristic length R_o replacing L_o. The important parameters are the activation criterion A, the thermicity criterion H, the thermal BIOT number B, and especially M, which appears as a THERMAL THIELE MODULUS

$$M = \frac{\mathfrak{R}^* L_o^2}{\alpha \rho} = \frac{t_T}{t_R} \tag{11}$$

where $\alpha = \lambda/(\rho c_p)$ is the thermal diffusivity

$t_R = \rho/\mathfrak{R}^*$ is a characteristic reaction time and $t_T = L_o^2/\alpha$ is a characteristic heat penetration time. If $M \ll 1$, $t_T \ll t_R$ so that heat has the time to penetrate into the particle before it volatilizes. Volatilization is thus controlled by the chemical reaction, this is the so-called CHEMICAL REGIME. If $M \gg 1$, $t_T \gg t_R$, heat has not the time to reach the particle core and volatilization takes place in a thin layer close to the surface. The rate of volatilization is controlled by an irreducible coupling between reaction and heat diffusion: this is the so-called ABLATION REGIME. We shall see below that shrinking then proceeds at a constant linear velocity.

2. Examples of simulations

Equations (6) to (10) and their equivalent for a sphere were solved numerically, yielding internal velocity and temperature profiles and time θ_F for total consumption as a function of physical parameters.

In the simulations reported here, the following values were selected:

392

$Y_p = Y_1 = 1$, $Y_o = 0.25$ (for instance $T_o = 300$ K and $T_p = T^{\#} = 1200$ K)

H = 0.5, A variable (1, 10, 100)

M and B variable.

Figure 1 shows internal temperature profiles, mainly for a 50 % linear size reduction (e.g. $\ell = 0.5$) in the case of Fourier (c) and Cauchy (a) conditions. The influence of M is obvious. When M is small, the temperature tends to become uniform whereas when M is large (M > 100), a steep temperature profile exists close to the surface. This is especially clear for constant surface temperature (Cauchy condition, B = ∞). In this case, a comparison between curves drawn for $\ell = 0.75$ and $\ell = 0.5$ shows that the temperature profile is simply translated as a function of time when volatilization proceeds, the core of the particle remaining cold. The influence of the Biot number B is also interesting: it appears that the ablation regime is more difficult to reach (even for large M) if the rate of heat transfer at the surface is slow (small B). Figures 2 to 4 show the reduction of size of particles (L/L_o or R/R_o) as a function of reduced time θ. Starting from the chemical regime (M = 0), where $L/L_o = \exp(-\theta)$, the decay curves tend to become straight lines in frankly established ablation regime (M > 100, B = ∞): $L/L_o = 1 - \theta/\theta_F$. Times for total consumption θ_F are reported as a function of M in figures 5 and 6. Several interesting remarks can be made by inspection of these figures:

- θ_F increases when M augments and when B diminishes (Fourier condition).

- Curves for different shapes are very close to each other for equal values of the Biot number B.

- As B $\to$ ∞, the Fourier condition tends to the Cauchy condition. In ablation regime, θ_F then tends to be proportional to $\sqrt{M}$.

For A = 10 and H = 0.5, one finds approximately

$$\theta_F \approx 3 \sqrt{M} \tag{12}$$

In dimensional variables,

$$t_F \approx 3 \sqrt{t_R t_T} = 3 L_o \sqrt{\frac{t_R}{\alpha}} \tag{13}$$

This means that the time for total consumption is proportional to the initial size and that the shrinking velocity is constant (a clue for the ablation regime). This also makes it possible to determine the true value of the reaction time t_R even in the presence of a severe heat transfer control. A value for the thickness of the reaction zone may be obtained as the ratio $e = \alpha/|u| \approx \alpha t_F/L_o$ of the heat diffusivity to the shrinking velocity. Then,

$$e \approx 3 \sqrt{\alpha t_R} \tag{14}$$

and

$$e/L_o \approx 3 L_o/\sqrt{M} \tag{15}$$

For instance, if M = 10 000, $e \approx 0.03$ L_o

- Coefficient 3 in relationships (12), (13), (14), (15) obviously depends on the numerical values of A, H and Y_o selected for simulations. Figure 6 shows that the absolute value of θ_F depends on A but that the curves are roughly parallel. It can be expected that in ablation regime, the $\sqrt{M}$ dependency still holds whatever the value of A.

In a previous paper [6], an empirical expression for θ_F in ablation regime and variable H has been established:

$$\theta_F \approx 1.13 (H + 2.3) \sqrt{M} \tag{16}$$

(A = 10, $Y_o = 0.25$, Cauchy condition)

However, this relationship should be checked by more careful numerical studies.

3. Conclusion

Although relying on very simple assumptions, the VTP model makes it possible to estimate the rate of consumption of solid particles as a function of physico-chemical parameters. Evidence for the existence of two volatilization regimes is provided, depending on the value of the thermal Thiele Modulus M and the thermal Biot number B. The ablation regime is achieved if both $M = t_T/t_R$ and $B = hL_o/\lambda$ are large (M, B > 100). In this regime, the shrinking velocity is constant and the reaction takes place only in a thin layer at the solid surface. Experimental data on wood pyrolysis obtained with sawdust or with massive rods confirm the existence of these two regimes (see companion paper). Total consumption times estimated in a cyclone reactor or direct measurement of ablation velocities are in agreement with theoretical predictions of the VPT model.

Example: For wood particles, $\lambda = 0.2$ W m^{-1} K^{-1}, $c_p = 2800$ J.kg^{-1}.K^{-1}, $\rho = 500$ kg.m^{-3}, $\alpha = 1.4 \times 10^{-7}$ m^2 s^{-1}, H = 0.5 corresponds to $\Delta H = 1680$ kJ.kg^{-1} at $T^* = 1200$ K. Then, $t_T = L^2/\alpha \approx 7 \times 10^{-2}$ s. For particles of $L_o \approx 10^{-4}$ s, the ablation regime requires that (M > 100) $t_R < 7 \times 10^{-4}$ s. If $t_R = 7 \times 10^{-4}$ s, then $t_F = 3 t_R \sqrt{M} = 30 t_R = 21 \times 10^{-3}$ s.

These preliminary results have been obtained with very simple numerical methods which are not best adapted to the "stiff" conditions encountered in the ablation regime (M and B both large). Further improvements are in progress, which will make it possible to perform more accurate simulations in a broader range of variation of parameters.

Literature cited

[1] Szekelly J., Evans J.W. and John H.Y. Gas Solid Reactions, Academic Press, 1976
[2] Levenspiel O. The Chemical Reactor Omnibook O.S.U., Corvallis, Oregon USA, 1979
[3] Hicks B.L. Theory of ignition considered as a thermal reaction. J. Chem. Phys. 22, (1954), 414
[4] Kindelan M., and Williams F.A. Theory for endothermic gasification of a solid by a constant energy flux. Comb. Sci. Technology, 10 (1975), 1
[5] Bradley H.H. Jr. Theory of ignition of a reactive solid by constant energy flux. Comb. Sci. Technol. 2 (1970), 11
[6] Villermaux J. and Antoine B. Pyrolyse éclair de solides divisés dans un réacteur continu. 1. Un nouveau modèle de volatilisation thermique de particules solides. Rev. Gen. Therm. Fr. n° 227, Nov. 1980, 851
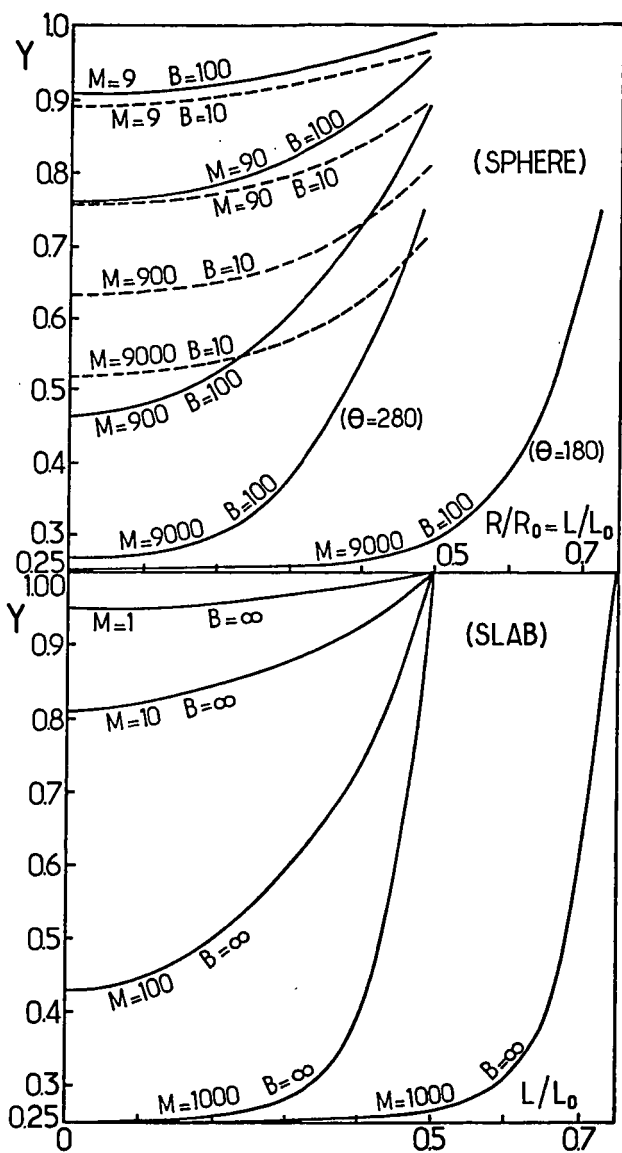
Fig. 1. Internal temperature profiles as a function of M and B (sphere and slab), mainly for $L/L_0 \gtrsim 0.5$. Notice the translation of the profile in ablation regime ($L/L_0 = 0.75 \to L/L_0 = 0.5$). A = 10, H = 0.5, $Y_0 = 0.25$
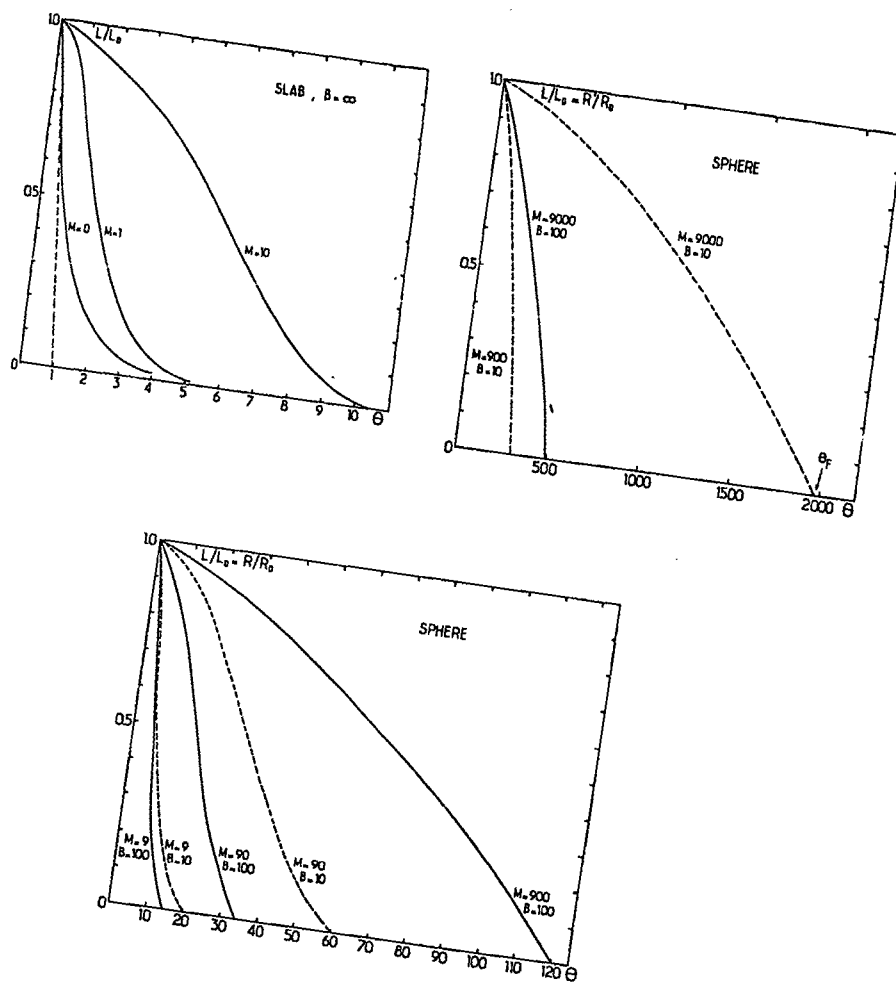
395

Fig. 2,3,4. Decrease of the particle size (L/L_0) as a function of time θ. Various shapes and conditions. $A = 10$, $H = 0.5$, $Y_0 = 0.25$.
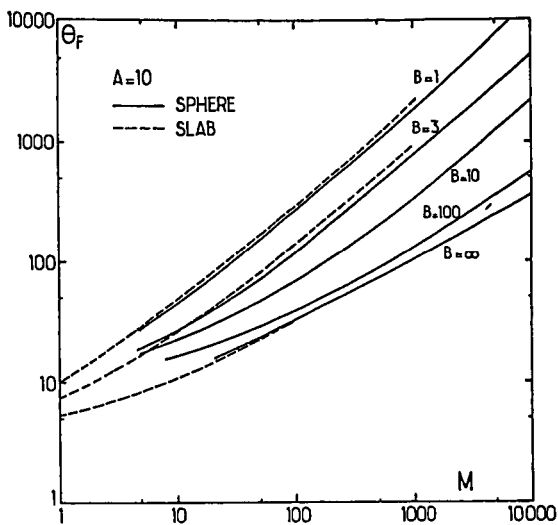
Fig. 5. Time for total consumption θ_F as a function of thermal Thiele modulus M. Various shapes and Biot numbers B (Fourier and Cauchy conditions). Notice the $\sqrt{M}$ dependency in ablation regime. A = 10, H = 0.5, Y_o = 0.25.
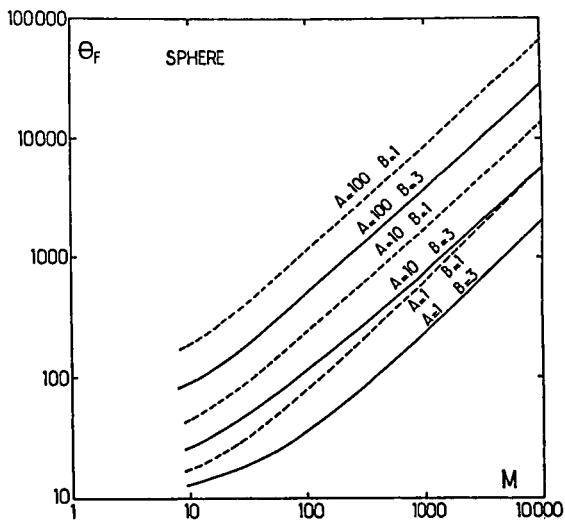

Fig. 6. Time for total consumption θ_F as a function of thermal Thiele modulus M. Influence of activation parameter A. H = 0.5, Y_o = 0.25.